

VI. "Note on Dulong and Petit's Law of Cooling." By DONALD MACFARLANE. Communicated by Prof. Sir W. THOMSON, F.R.S. Received June 10, 1875.

The 'Journal de Physique' for December 1873 contains a friendly notice by Professor A. Cornu of experiments made to determine surface-conductivity for heat (or, as we may call it, "thermal emissivity") in absolute measure, an account of which was communicated to the Royal Society, and read January 1872 (see Proceedings, vol. xx. p. 90). On the results there given M. Cornu remarks:—

"Ces nombres vérifient la conclusion de Dulong et Petit, à savoir que les vitesses de refroidissement ne dépendent de l'état des surfaces que par une constante de proportionalité.

"L'accélération négative du rapport des pouvoirs émissifs n'infirmes pas sensiblement cette conclusion; elle est si faible qu'elle peut être attribuée à une petite erreur régulière dans l'évaluation des différences de température; en effet, l'auteur ne paraît tenir aucun compte d'une cause délicate d'erreur qui avait préoccupé Dulong et Petit, à savoir la résistance inégale à la transmission de la chaleur dans les deux cas. Il est évident que, dans le refroidissement le plus rapide, la température est distribuée moins uniformément que dans le cas d'un refroidissement lent; l'aiguille thermoélectrique indique donc moins bien la température moyenne de la masse que les boules de mercure des physiciens français."

On this it is to be remarked that a rigorous proportionality in the rates of cooling of different surfaces is in itself not probable; and my experiments in fact disprove it, so far as it is not at all likely that the errors of observation could be so great or so consistently regular in the same direction as the truth of the supposed law would require.

As to the variation of temperature from centre to surface occasioned by the rapid cooling of the ball, this was certainly not overlooked in planning the experiments. Sir William Thomson considered the matter carefully, and selected copper, on account of its high conductivity, estimating that in a copper ball of the dimensions used (diameter 4 centimetres) the temperature must be sensibly uniform throughout. A very simple calculation (made in consequence of M. Cornu's criticism, and appended below) from Fourier's celebrated formula for the cooling of a homogeneous solid globe shows, in fact, that, in the case of a copper globe of 2 centimetres radius, the centre is warmer than the surface by only about  $\frac{1}{4000}$  of the excess of its temperature above that of the surrounding medium. There would be a much greater difference of temperature between surface and centre in a globe of mercury of the same dimensions, because mercury is a much worse conductor of heat than copper, and because a much greater difference of temperatures than that which there is in the copper would be required to produce any considerable convection of heat by currents in the liquid. Moreover the glass envelope con-

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taining the mercury in a thermometer-bulb of ordinary dimensions produces a sensible difference of temperature between the outer surface of the glass exposed to the external medium and the surface of the mercury. For let  $b$  be the thickness of the glass,  $E$  the "emissivity" of its outer surface, and  $k$  the conductivity of its substance; let the excess of temperature of the outer surface of the glass above that of the surrounding medium be  $v$ , and the excess of temperature of the inner surface of the glass above the outer  $\delta v$ ; we have

$$k \frac{\delta v}{b} = Ev.$$

Now by the Glasgow experiments it has been found that  $E$  is approximately  $\frac{1}{4000}$  of a gramme-water thermal unit per square centimetre per second; and by the determinations of conductivities of stones and underground strata in absolute measure by Peclet and Forbes the value of  $k$  for glass may be roughly estimated at  $\frac{1}{400}$ , in terms of centimetre, second, and gramme-water thermal unit. Hence

$$\frac{\delta v}{v} = \frac{1}{10} b.$$

Thus, if the thickness of the glass be half a millimetre (i. e.  $b = \frac{1}{20}$ ), we have

$$\delta v = \frac{1}{200} v.$$

This is a small difference, but by no means imperceptible in the delicate experiments of Dulong and Petit; and it is twenty times the difference of temperature between the centre and surface of the cooling copper globe of 4 centimetres diameter.

#### APPENDIX.

Distribution of temperature in a cooling copper globe of 4 centimetres diameter, calculated from Fourier's formula

$$v = \sum P_i \frac{\sin \theta_i}{\theta_i} e^{-\rho_i^2 t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$\rho_i = \frac{\omega_i^2 k}{a^2 c}, \quad \theta_i = \frac{x}{a} \omega_i,$$

$\omega_i$  roots of the transcendental equation

$$\frac{\omega}{\tan \omega} = 1 - \frac{Ea}{k}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and  $P_i$  coefficients determined to give (according to Fourier's method)

any arbitrary function of  $x$  from  $x=0$  to  $x=a$ , for the value of  $v$ , when  $t=0$ :

$v$  temperature at time  $t$  and distance  $x$  from centre of globe,

$a$  the radius of the globe,

$k$  the thermal conductivity of its substance,

$c$  the thermal capacity per unit volume of its substance,

$E$  the thermal emissivity of its surface.

Taking centimetre, second, and gramme-water thermal units for the fundamental units, we have, as stated above,

$$E = \frac{1}{4000} \text{ (rough approximation);}$$

and Ångström's experiments gave for copper

$$k = 1 \text{ approximately.}$$

Therefore

$$\frac{Ea}{k} = \frac{a}{4000};$$

and for the globe of 4 centimetres diameter used in the Glasgow experiments,

$$\frac{Ea}{k} = \frac{1}{2000}.$$

In all cases in which  $\frac{Ea}{k}$  is small, the smallest root of the transcendental equation (2) is approximately equal to

$$\sqrt{\frac{3Ea}{k}}.$$

Calling this  $\omega_1$ , we have

$$\rho_1 = \frac{3E}{ac}$$

and

$$\begin{aligned} \frac{\sin \theta_1}{\theta_1} &= 1 - \frac{1}{6} \theta_1^2 \text{ approximately,} \\ &= 1 - \frac{1}{2} \frac{Ea}{k} \frac{x^2}{a^2}. \end{aligned}$$

Now any chosen term of (1) is a particular solution of the problem; that is to say, it is *the* solution for the case for which the initial distribution of temperature is that which it expresses when  $t=0$ . Hence

$$v = \left( 1 - \frac{1}{2} \frac{Ea}{k} \frac{x^2}{a^2} \right) e^{-\frac{3E}{ac}t}$$

expresses the temperature at time  $t$ , if when  $t=0$  the temperature is expressed by

$$v = 1 - \frac{1}{2} \frac{Ea}{k} \frac{x^2}{a^2}.$$

Taking, for instance, the copper globe of 4 centimetres diameter, we have

$$v = \left(1 - \frac{1}{4000} \frac{x^2}{a^2}\right) e^{-\frac{3E}{ac}t}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and we see that in the Glasgow experiments the difference of temperatures between surface and centre was just  $\frac{1}{4000}$  of the excess of either above the temperature of the surrounding medium, when time enough had elapsed to allow the first term of Fourier's series to be the predominating one. *Before* that time the difference of temperatures must have been *less* than  $\frac{1}{4000}$  of either, if initially the temperature was uniform from surface to centre. The Fourier analysis of the transition from the supposed initial uniform distribution to the state represented by (3) is exceedingly interesting, but unnecessary for the settlement of the present question.

VII. "Preliminary Results of an Investigation on the Electric Conductivity of Glass at different Temperatures." By JOHN PERRY, B.E., Thomson Experimental Scholar in The Natural Philosophy Laboratory at Glasgow\*. Communicated by Professor Sir WILLIAM THOMSON, F.R.S., LL.D. Received April 8, 1875.

A quadrant electrometer now in use in the laboratory seems to retain its whole charge from day to day; a week's loss is just perceptible, and may be supplied by a few turns of the replenisher. In a guard-ring electrometer now in use the charge is almost wholly retained from week to week. These qualities are due to the exceptionally great insulation-resistance of the glass employed.

At various times experiments have been made in the laboratory at Glasgow to determine the insulation-resistance of different kinds of glass. Of the specimens hitherto examined, those of flint glass have insulated best; and it is hoped that experiments on flint glass now being proceeded with will define the most suitable glass for use in electrometers and other electrical instruments.

The method of investigation is essentially the same as that which was adopted by Sir William Thomson some years ago. B D A (fig. 1) is a

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